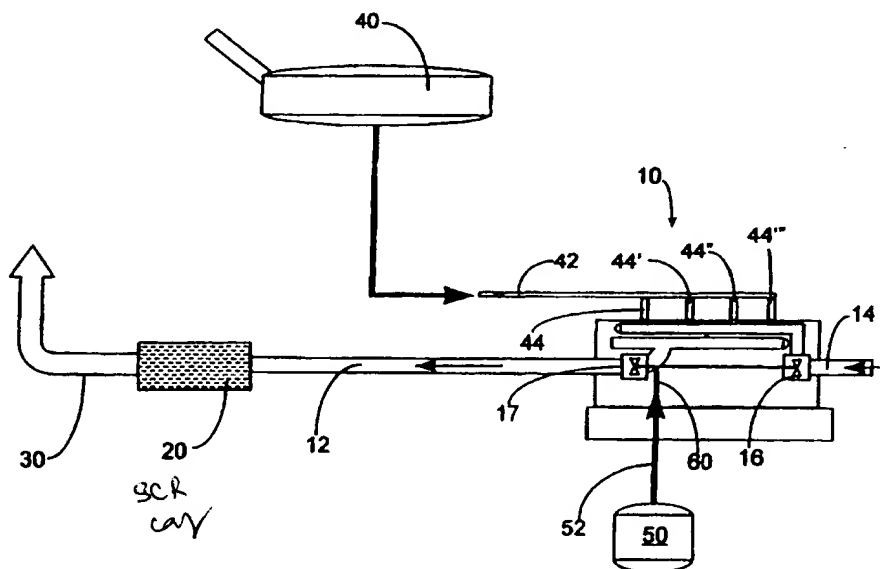


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<b>(21) International Application Number:</b> PCT/US97/05468 <b>(22) International Filing Date:</b> 2 April 1997 (02.04.97) <b>(30) Priority Data:</b> 08/626,780      2 April 1996 (02.04.96)      US <b>(71) Applicant (for all designated States except US):</b> CLEAN DIESEL TECHNOLOGIES, INC. [US/US]; Suite 702, 300 Atlantic Street, Stamford, CT 06901-3522 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> PETER-HOBLYN, Jeremy, D. [GB/GB]; Lamellon St. Tudy Bodmin, Cornwall PL30 3NR (GB). VALENTINE, James, M. [US/US]; 480 Hemlock Road, Fairfield, CT 06430 (US). SPRAGUE, Barry, N. [US/US]; 82 Longmeadow Road, Bethlehem, CT 06751 (US). <b>(74) Agents:</b> CARVIS, Thaddius, J. et al.; St. Onge Steward Johnston & Reens L.L.C., 986 Bedford Street, Stamford, CT 06905-5619 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** METHOD AND APPARATUS FOR REDUCING HARMFUL EMISSIONS FROM A DIESEL ENGINE BY UREA INJECTION SCR

**(57) Abstract**

Emission of NO<sub>x</sub> from diesel engines is reduced by hydrolyzing or otherwise gasifying urea on an as-needed basis. Preferably, an aqueous urea solution is introduced into a catalyzed chamber (60) maintained at least partially in contact with the exhaust system (12). The heat of the exhaust gases is utilized to gasify the urea. The gaseous breakdown products of the urea are then introduced into the exhaust gases upstream of an SCR catalyst. In one form of the invention, an oxidation catalyst (22) is provided down stream of the SCR catalyst (20) for the purpose of eliminating any ammonia which might otherwise pass through the system and provide an objectionable odor.

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## DESCRIPTION

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### METHOD AND APPARATUS FOR REDUCING HARMFUL EMISSIONS FROM A DIESEL ENGINE BY UREA INJECTION SCR

#### Related Applications

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This application is a continuation-in-part of copending and commonly-assigned U.S. Patent Application No. 08/518,251 entitled Method for Reducing Emissions of NO<sub>x</sub> and Particulates from a Diesel Engine, filed August 23, 1995, by J. D. Peter-Hoblyn, which in turn is a continuation of copending and commonly-assigned U.S. Patent Application No. 08/089,838 filed July 12, 15 1993. The first of these was filed internationally and the PCT application was published as WO 95/02655 on January 26, 1995.

#### 20 Technical Field

Diesel engines produce NO<sub>x</sub> and particulates during normal operation. In fact, there is a tradeoff between these two forms of pollution. When primary measures are taken to reduce one, the other is usually increased. 25 Primary measures are actions which affect the combustion process itself. These include exhaust gas recirculation, engine timing adjustments, and the introduction of water such as by means of fuel-water emulsions.

This invention provides a means and a method for reducing the 30 emissions of NO<sub>x</sub> from diesel engines, particularly those used to power land and water vehicles. The invention enables the use of primary means to reduce particulate generation to low levels and to utilize SCR (selective

catalytic reduction) as a secondary measure to reduce NO<sub>x</sub>. Secondary measures reduce the pollutant after it is generated. The invention avoids the safety problems of carrying ammonia while, at the same time, eliminating the need for complex urea mixing chambers and the possible fouling of a NO<sub>x</sub>-  
5 reducing catalyst by urea.

Primary measures for NO<sub>x</sub> reduction have shortcomings in addition to their effect on particulate generation. For example, while fuel-water emulsions have been found to provide significant reductions in NO<sub>x</sub> formation  
10 and emission, they negatively impact power and drivability. Moreover, the amount of water necessary to achieve this result can significantly add to the required fuel storage capacity. In retrofit situations, this can be a limiting factor. Likewise, exhaust gas recirculation cannot be easily added to an  
15 existing diesel-powered vehicle. And, engine timing adjustments can provide modest NO<sub>x</sub> reductions only by causing the generation of increased amounts of particulates.

Among the known secondary means for reducing NO<sub>x</sub>, are SCR systems utilizing catalysts which are active when a NO<sub>x</sub>-reducing agent is  
20 mixed with the combustion gases prior to contact with the catalyst. Ammonia is an effective NO<sub>x</sub>-reducing agent but is generally considered too hazardous for use in mobile diesel operations. Urea has also been tested; however, it has been difficult to employ without having a portion of it pass  
through the exhaust system and into the SCR catalyst chamber without being  
25 broken down. This is because, at the temperatures typical for diesel exhaust, the urea decomposes to form solid byproducts which can result in catalyst fouling, limiting the efficiency of the catalyst and increasing the back pressure on the engine.

There is a current need for a safe, economical and effective answer to these interrelated problems.

## 5 Background Art

Diesel engine exhaust is a principal deterrent to the more wide-spread use of these efficient power sources. However, until technology becomes available for controlling NO<sub>x</sub> without unduly increasing particulate emissions, gasoline-fueled engines will continue to dominate the scene for mobile water and land use. This is not the best environmental choice, however, because gasoline engines tend to be less efficient and less reliable. A gasoline engine emits more carbon monoxide than a diesel for the same power output.

As noted above, a number of primary measures have been attempted for the purpose of reducing the formation of NO<sub>x</sub> by diesel engines. However, such measures cannot be successful to the extent now seen as necessary. Selective catalytic reduction (SCR) utilizing ammonia has had some degree of success as a secondary measure for stationary sources of NO<sub>x</sub>, but would be too dangerous for mobile use.

In U. S. Patent No. 3,900,554, Lyon discloses that ammonia can be used to reduce NO<sub>x</sub> in a noncatalytic system, now termed selective noncatalytic reduction (SNCR). This process cannot achieve the 90% and above reductions that are possible with catalysts, but has been considered an improvement over SCR in situations where high reductions are not critical. The danger of dealing with ammonia, however, remains a problem. Moreover, the temperature of diesel exhaust does not reach that (above 1600°F) necessary for SNCR.

In U. S. Patent No. 4,208,386, Arand and Muzio disclose that urea, like ammonia, can be employed for SNCR systems. However, the same temperature limitation exists.

5       The application of urea SCR technology to diesel engines risks fouling the catalysts under most conditions. The costs which could result would be prohibitive, even if regulatory approval could be obtained, knowing that shut down would reduce projected reliability. If an SCR system were to require frequent shutdowns, it may not be considered suitable technology.

10

      The limited attempts to use urea SCR for diesel engines has required the use of large pyrolyzation chambers, as disclosed in European patent specification 558,452 A1. Equipment of this type is bulky and expensive, and is often not practical from an engineering standpoint, especially for road  
15       transport application. Also, see PCT publication WO 95/518,251, by J. D. Peter-Hoblyn. That application calls for use of a diesel particulate trap, with urea being introduced into the exhaust gases before entering the trap. That disclosure notes that it was possible for the trap to collect the urea which had not been fully dissociated before reaching the trap and hold it there, with the  
20       particulates, until all urea was reduced to gaseous form such that it could be of use in an SCR section.

      Urea hydrolysates have been identified as alternatives to urea in several contexts. See for example, U.S. Patent No. 4,997,631 to Hofmann, *et al.*,  
25       PCT application WO 92/02291 to von Harpe, *et al.*, and U. S. Patent No. 5,139,754, Hofmann, Sun and Luftglass. Also see U. S. Patent No. 5,281,403 to Jones and JP HEI 2-191,528 to Ebina. Each of these requires the use of added hydrolysis equipment and ends up producing ammonia to some extent. On-board storage of hydrolysates would, of course, be undesirable.

30

The art as it now stands continues to look at ammonia as the most suitable chemical for SCR processes -- just as it has for the past several decades -- whether in gaseous form as traditionally employed or as an aqueous solution prepared by the complete hydrolysis of urea. The art so far  
5 has failed to meet the need for a system for supplying ammonia gas safely to the effluent in the area of the catalyst.

The use of ammonia in the manner of the prior art -- whether as a gas, aqueous solution or a hydrolysate -- is not only expensive, it does not  
10 eliminate the possibility of leakage and the associated health and safety problems. The development of a process which would permit the use of urea in an SCR process simply, reliably, economically and safely for both man and catalyst is an advance the art is awaiting.

15

### **Disclosure of Invention**

It is an object of the invention to provide a safe, reliable SCR system for a mobile diesel engine.

20

It is another object of the invention to eliminate the safety problems associated with the storage and handling of ammonia for mobile uses.

It is another object of the invention to permit the introduction of urea  
25 into combustion gases of a diesel engine at temperatures suitable for SCR, without fear of catalyst fouling due to the deposition of urea or its incomplete breakdown products.

It is another object of the invention to enable the protection of SCR  
30 catalysts so effectively that urea can be employed over a wide temperature

window without causing deposits on the catalyst which reduce its effectiveness and increase back pressure on the engine.

It is yet another and more specific object of the invention to eliminate  
5 the dangers associated with the use of ammonia for reducing emissions of  $\text{NO}_x$  from diesel engines by the use of urea with an SCR system.

It is yet another, more specific object of the invention to eliminate the need for a diesel trap by operation under conditions which reduce the  
10 particulates to acceptably low levels, preferably less than 0.05 grams per horsepower-hour, and then reducing the  $\text{NO}_x$  by the use of a safe SCR system utilizing urea.

It is yet another specific object of the invention to provide a simple  
15 mechanical device for accomplishing the above objects.

These and other objects are achieved by the present invention which provides an improved process and apparatus for  $\text{NO}_x$  reduction. The process, in one of its aspects comprises hydrolyzing or otherwise gasifying  
20 urea on an as-needed basis, preferably by: introducing an aqueous urea solution into a catalyzed chamber maintained at least partially in contact with the exhaust system, utilizing the heat of the exhaust gases to gasify the urea, and introducing the urea into the exhaust gases upstream of an SCR catalyst. In one embodiment of the invention, an oxidation catalyst is  
25 provided downstream of the SCR catalyst for the purpose of eliminating ammonia which might otherwise pass through the system and provide an objectionable odor.



### Brief Description of the Drawings

The invention will be better understood and its advantages more apparent from the following detailed description, especially when read in  
5 light of the accompanying drawings, wherein:

Figure 1 is a schematic representation of one embodiment of the invention;

Figure 2 is a schematic representation of a preferred form of gasification catalyst chamber according to the invention; and

10 Figure 3 is a schematic representation, similar to that of Figure 1, but with the provision of a control system and an oxidation catalyst in the exhaust system to prevent inadvertent release of large amounts of ammonia gas.

### 15 Detailed Description of the Preferred Embodiment

Reference is made to Figure 1 which illustrates in schematic form one embodiment of the invention wherein the exhaust from a diesel engine 10 is treated to reduce  $\text{NO}_x$ . The invention concerns diesel engines equipped with  
20 or having associated therewith an exhaust system having an exhaust passage, such as 12, leading to a catalytic reactor, such as SCR unit 20, effective for selective catalytic  $\text{NO}_x$  reduction. The invention enables utilization of urea for SCR  $\text{NO}_x$  reduction by gasifying it in a catalyzed gasification chamber 60 which includes at least one catalyst material  
25 effective for breaking down urea by hydrolysis and/or pyrolysis.

In this description, the term "diesel engine" is meant to include any of those engines capable of being run on "diesel fuel", as defined by the American Society of Testing and Management (ASTM) Standard

Specification for Fuel Oils (designation D 396-86) or any of grade numbers 1-D, 2-D or 4-D, as specified in ASTM D 975. More generally, diesel fuel can be a fuel oil No. 2 or No. 4 petroleum distillates as well as alternative diesel fuels containing emulsified water or alcohols such as ethanol or methanol, very  
5 low sulfur fuels (less than 0.05% sulfur), diesel fuel blends with bioderived components (animal and vegetable fats and oils, fractions and derivatives), and the like, as long as they exhibit volatility and cetane number characteristics effective for the purpose. Diesel fuels will typically have a 90% distillation point within the range of 300° to 390°C and a viscosity of from 1 to 25  
10 centistokes at 40°C.

Figure 1 shows a diesel engine 10 having an exhaust manifold/passage 12 directing the exhaust from the engine to an exhaust system including a NO<sub>x</sub>-reducing SCR catalyst 20 ahead of a tail pipe 30 through which the  
15 combustion gases are exhausted to the atmosphere. The diesel engine is supplied with fuel from tank 40 via line 42 and fuel injectors 44, 44', 44", and 44' ". The fuel tank includes diesel fuel and can contain a platinum group metal catalyst composition and/or an auxiliary catalyst composition as will be explained later. Combustion air from line 14 enter turbine 16, and is  
20 introduced into the cylinders of the diesel engine and compressed in normal fashion for a diesel engine within each cylinder. For modern, high-performance diesel engines it is typical to employ a turbine to pressurize the combustion air and to utilize the heat from the exhaust gas to heat the combustion air prior to introduction into the cylinders. Turbine 16 is driven by  
25 turbine 17 positioned in exhaust line 12. The diesel fuel (optionally catalyzed as described below) is injected into the cylinders where it ignites in the presence of the air which has been heated due to compression within the cylinders. Desirably, a static mixer (not shown) is positioned between the gasification chamber and the NO<sub>x</sub>-reduction catalyst.

The arrangement of Figure 1 enables reducing the emissions of  $\text{NO}_x$  from a diesel engine by hydrolyzing and/or pyrolyzing, or otherwise gasifying urea on an as-needed basis. An aqueous urea solution is introduced from tank 50, through line 52 into catalyzed gasification chamber 60 maintained at least partially in contact with the exhaust system, utilizing the heat of the exhaust gases to gasify the urea, and introducing the urea into the exhaust gases upstream of an SCR catalyst. Additional heat for gasification can be supplied by an electric heater as can be seen better in Figure 2. The arrangement illustrated shows gasification chamber 60 to be located before the outlet vanes 17 of a turbocharger. This is one of the preferred orientations, another being centrally within exhaust passage 12 (not shown). The gasification chamber will preferably contain at least one catalyst capable of aiding pyrolysis of the urea and/or aiding hydrolysis of the urea.

Figure 2 shows a gasification chamber 60 according to the invention, in greater detail than shown in Figure 1. The downstream end of chamber 60 has an outlet member 62 which is preferably a foraminous element and can comprise the pyrolysis catalyst. Desirably, a catalyst which aids hydrolysis of urea resides in the chamber 60 into which the aqueous urea is introduced via line 52. If desired it can also contain a catalyst which aids the pyrolysis of the urea.

Among the catalysts suitable for aiding the hydrolysis of the urea (*i.e.*, the hydrolysis catalysts) are ones which comprise a material selected from the group consisting of phosphoric acid and acid phosphates, alkali metal hydroxides and carbonates, such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, alkali metal silicates, alkaline earth metal hydroxides, aluminum hydroxide, and mixtures of two or more of these. Preferred catalysts of this type are those which comprise water-soluble

materials which is added to or blended with the urea in tank 50 or otherwise prior to being introduced into the gasification chamber.

Among the suitable catalysts for aiding the pyrolysis of the urea (*i.e.*,  
5 the pyrolysis catalysts) are ones which comprise a material selected from the group consisting of platinum group metals, such as palladium and platinum, stainless steel, and the oxides of vanadium, chromium, titanium, molybdenum and nickel, and mixtures of two or more of these. The pyrolysis catalyst preferably comprises one of these materials in a foraminous  
10 configuration, e.g., a form selected from the group consisting of wire mesh, sintered metal, sheet metal with mechanically formed holes, zeolite, alumina, ceramic, beads, honeycomb structures, rings and saddles. These or other materials can be impregnated or coated with catalytic material.

15 The net effect of the gasification is a breakdown of the urea into ammonia gas or ammonium carbonate, ammonium bicarbonate, ammonium carbamate, or the like, in aqueous solution. The evaporation of the water and the gasification of the urea upon introduction into the gasification chamber have the advantage that no atomizing air is required.  
20 Urea residues not hydrolyzed are broken down by the pyrolysis catalyst so that they do not enter the SCR catalyst.

The urea is typically supplied as an aqueous solution containing from 25 to 50% urea by weight. It can be stored in tank 50 in this form or the urea  
25 can be stored dry in a canister, with water passed through as needed to prepare a solution which is near saturation (to minimize water storage and use) or to any concentration suitable for the vehicle. It will be desired in many circumstances to provide heaters for the water and/or urea solution storage to prevent freezing or to reduce reaction time in the gasification  
30 chamber. Likewise, it may be useful to employ antifreeze materials.

The aqueous urea solution can be fed into the gasification chamber in response to fuel flow. For example, reference to Figure 3 shows a control system including flow meter which 72 can sense the fuel flow and generate a signal representative of fuel flow. The signal representative of fuel flow is the received by a controller 74 and compared to stored values. The controller can then generate a control signal based on the comparison. The control signal is then sent to metering pump 76 or other suitable device for metering the correct amount of urea to gasification chamber 60 via line 52.

Advantageously, the urea is introduced into the gasification chamber in an amount sufficient to provide a molar ratio of the ammonia generated to the baseline nitrogen oxides level (by which is meant the pre-treatment level of  $\text{NO}_x$  in the effluent) of about 0.5:1 to about 1.5:1. More preferably, treatment solution is introduced into the effluent to provide a molar ratio of ammonia to baseline nitrogen oxides of about 1:1 to about 1.2:1, most preferably about 1:1. The  $\text{NO}_x$  levels can be preprogrammed into the controller 74 based on tested  $\text{NO}_x$  values for given fuel flows and related parameters, or a sensor and related controls can be provided to provide real-time readouts. Preferably, a sensor means is provided to correct preprogrammed values.

The SCR catalyst used is one capable of reducing the effluent nitrogen oxides concentration in the presence of ammonia. These include, for instance, activated carbon, charcoal or coke, zeolites, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, copper oxide, manganese oxide, chromium oxide, noble metals such as platinum group metals like platinum, palladium, rhodium, and iridium, or mixtures of these. Other SCR catalyst materials conventional in the art and familiar to the skilled artisan can also be utilized. These SCR catalyst materials are typically mounted on a support

such as a ceramic substance, a zeolite, or a homogeneous monolith, although other art known supports can also be used.

Among the useful SCR catalysts are those described in the  
5 representative prior art processes below. Selective catalytic reduction processes for reducing NO<sub>x</sub> are well known and utilize a variety of catalytic agents. For instance, in European Patent Application WO 210,392, Eichholtz and Weiler discuss the catalytic removal of nitrogen oxides using activated charcoal or activated coke, with the addition of ammonia, as a catalyst.  
10 Kato *et al.* in U.S. Patent 4,138,469 and Henke in U.S. Patent 4,393,031 disclose the catalytic reduction of NO<sub>x</sub> using platinum group metals and/or other metals such as titanium, copper, molybdenum, vanadium, tungsten, or oxides thereof with the addition of ammonia to achieve the desired catalytic reduction.

15  
Another catalytic reduction process is disclosed by Canadian Patent 1,100,292 to Knight which relates to the use of a platinum group metal, gold, and/or silver catalyst deposited on a refractory oxide. Mori *et al.* in U.S. Patent 4,107,272 discuss the catalytic reduction of NO<sub>x</sub> using oxysulfur, sulfate,  
20 or sulfite compounds of vanadium, chromium, manganese, iron, copper, and nickel with the addition of ammonia gas.

In a multi-phased catalytic system, Ginger, in U.S. Patent 4,268,488, discloses exposing a nitrogen oxides containing effluent to a first catalyst  
25 comprising a copper compound such as copper sulfate and a second catalyst comprising metal combinations such as sulfates of vanadium and iron or tungsten and iron on a carrier in the presence of ammonia.

The ammonia-containing effluent is most preferably passed over the  
30 SCR catalyst while the effluent is at a temperature between about 230°F and

about 950°F, preferably at least 550°F. In this manner, the ammonia present in the effluent by the introduction of the ammonium carbamate solution most effectively facilitates the catalytic reduction of nitrogen oxides. The effluent will preferably contain an excess of oxygen, e.g., from about 1 to about 10%.

5

Use of the present invention with any of the above SCR catalysts (the disclosure of which are specifically incorporated by reference) reduces or eliminates the requirement for the transport, storage and handling of large amounts of ammonia or ammonium water. Even where the inventive process does not provide all of the ammonia required for the catalytic reduction of nitrogen oxides, the reduction of the amount needed still provides significant advantages in terms of both safety and cost.

10

Figure 3 shows an arrangement similar to Figure 1, but includes an oxidation catalyst 22 downstream of the SCR catalyst 20 for the purpose of eliminating ammonia which might otherwise pass through the system and provide an objectionable odor. Among the catalysts suitable for this purpose are oxidation catalysts. If desired, the SCR catalyst can be preceded by an uncatalyzed support material or other trap to pick up any ungasified urea or particulate materials. It is an advantage of the invention that the use of such a device to further protect the catalyst is economical, but can provide the added safety needed to assure a high level of effectiveness. The uncatalyzed support material will typically have a volume of from 5 to 50% of that of the SCR catalyst.

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It is another advantage of the invention that the need for a diesel trap may be eliminated by operation under conditions which reduce the particulates to acceptably low levels, preferably less than 0.05 grams per horsepower-hour, and then reducing the NO<sub>x</sub> by the use of a safe SCR system utilizing urea.

30

The fuel can be catalyzed with a suitable platinum group metal additive and/or auxiliary catalyst composition selected from the group consisting of compounds of sodium, lithium, potassium, calcium, magnesium, cerium, iron, copper, manganese, and mixtures. Preferred among the platinum group metal catalyst compositions are those which are soluble in the typical diesel fuel which is essentially a nonpolar hydrocarbon fuel, but can contain tramp moisture in amounts which would destabilize some fuel-soluble platinum group metal compositions. Among these are hydrocarbon-fuel-soluble organometallic platinum group metal coordination compounds.

5 The compounds in this group are any of those disclosed for example in prior U.S. Patent Nos. 4,892,562 and 4,891,050 to Bowers and Sprague, 5,034,020 to Epperly and Sprague, 5,215,652 to Epperly, Sprague, Kelso and Bowers, and 5,266,083 to Peter-Hoblyn, Epperly, Kelso and Sprague, and WO 90/07561 to Epperly, Sprague, Kelso and Bowers. Reference can be made to these

10 disclosures for details of preparation and purification. Where the application permits, a blend of these compounds can be used with one or more other platinum group metal compounds such as soaps, acetyl acetonates, alcoholates,  $\beta$ -diketonates, and sulfonates, e.g., of the type which will be described in more detail below. Preferably, the composition will be

15 temperature stable, and substantially free of phosphorus, arsenic, antimony, or halides.

20

In addition to the highly fuel-soluble compounds that are stable in the presence of water, the invention makes use of platinum group metal catalyst compositions which would normally be taken up or destabilized by any water present. These platinum group metal catalyst compositions can be either simply water-sensitive or essentially water-soluble. Water-sensitive platinum group metal catalyst compositions are characterized as being instable in the presence of from about 0.01 to about 0.5% water, but having sufficient

25 affinity for the fuel that when a water-functional composition is employed,

30



they remain in the fuel and effective for their intended catalytic function. Among the platinum group metal catalyst compositions in this group are, alcoholates, sulfonates, substituted and unsubstituted beta-diketonates and soaps selected from the group consisting of stearates, palmitates, laurates, tallates, naphthanates, other fatty acid soaps, and mixtures of two or more of these.

The platinum group metal catalyst can be added in any manner effective, such as by adding it to the fuel in bulk storage, to the fuel in a tank associated with the engine, or by continuous or intermittent addition, such as by a suitable metering device, into: the fuel line leading to the engine, or in the form of a vapor, gas or aerosol into the air intake, the exhaust gases before the trap, exhaust gases after the trap but before recirculation to the engine, or a mixing chamber or equivalent means wherein the exhaust gases are mixed with incoming air.

The platinum group metal catalyst composition is preferably employed at a level of less than 1 part by weight of platinum group metal per million parts by volume fuel (ppm). For the purposes of this description, all "parts per million" figures are on a weight to volume basis, *i.e.*, grams/million cubic centimeters (which can also be expressed as milligrams/liter), and percentages are given by weight, unless otherwise indicated. Auxiliary catalysts are employed at levels effective for their intended purpose, preferably at levels of from 1 to 100 ppm of the fuel utilized, *e.g.*, 10 to 60 ppm.

When the catalyzed fuel is combusted, the catalyst metals are released in the combustion gases and are then passed to the SCR catalyst. This has the advantage that an added measure of reliability is provided by the addition of catalyst metal to the SCR support to maintain effectiveness

even in cases where there is some minor fouling due to particulates or other impurities in the combustion gases.

5       The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading this description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the  
10       following claims. The claims cover the indicated components and steps in all arrangements and sequences which are effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

**CLAIMS**

1. A method for reducing the emissions of NO<sub>x</sub> from a diesel engine having associated therewith an exhaust system having an exhaust passage leading to an SCR catalytic reactor effective for selective catalytic NO<sub>x</sub> reduction, comprising: introducing an aqueous urea solution into a catalyzed gasification chamber maintained at least partially in contact with the exhaust system, utilizing heat of the exhaust gases to gasify the urea in the gasification chamber, and introducing the urea into the exhaust gases upstream of an SCR catalyst.
2. A method according to claim 1 wherein an oxidation catalyst is provided down stream of the SCR catalyst for the purpose of eliminating ammonia which might otherwise pass through the system and provide an objectionable odor.
3. A method according to claim 1 wherein said catalyzed chamber includes at least one catalyst material effective for breaking down the urea.
4. A method according to claim 3 wherein said catalyst material within said chamber comprises a catalyst which aids the pyrolysis of the urea.
5. A method according to claim 3 wherein said catalyst material within said chamber comprises a catalyst which aids the hydrolysis of the urea.
6. A method according to claim 5 wherein said catalyst material within said chamber comprises a catalyst which aids the pyrolysis of the urea.
7. A method according to claim 6 wherein said catalyst which aids the hydrolysis of the urea comprises a material selected from the group consisting

of alkali metal hydroxides and carbonates, including sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, alkali metal silicates, alkaline earth metal hydroxides, aluminum hydroxide, and mixtures of two or more of these.

8. A method according to claim 7 wherein said catalyst which aids the hydrolysis of the urea comprises a water-soluble material which is added to or blended with the urea prior to being introduced into the gasification chamber.

9. A method according to claim 6 wherein said catalyst which aids the pyrolysis of the urea comprises a material selected from the group consisting of palladium, platinum, stainless steel and the oxides of vanadium, chromium, titanium, molybdenum and nickel, and mixtures of two or more of these.

10. A method according to claim 1 wherein the gasification chamber is heated by an auxiliary heat source.

11. A method according to claim 6 wherein said catalyst which aids the pyrolysis of the urea comprises a foraminous material selected from the group consisting of wire mesh, sintered metal, sheet metal with mechanically formed holes, zeolite, alumina, ceramic, beads, honeycomb structures, rings and saddles.

12. A method according to claim 11 wherein said catalyst is impregnated into or coated on said foraminous material.

13. A method according to claim 1 wherein a section of uncatalyzed support material, an oxidation chamber or a particulate trap precedes the gasification chamber.
14. A method according to claim 1 wherein the urea is metered into the gasification chamber is positioned between the exhaust valves of the engine and a turbocharger outlet fan.
15. A method according to claim 1 wherein a static mixer is positioned between the gasification chamber and the NO<sub>x</sub>-reduction catalyst.

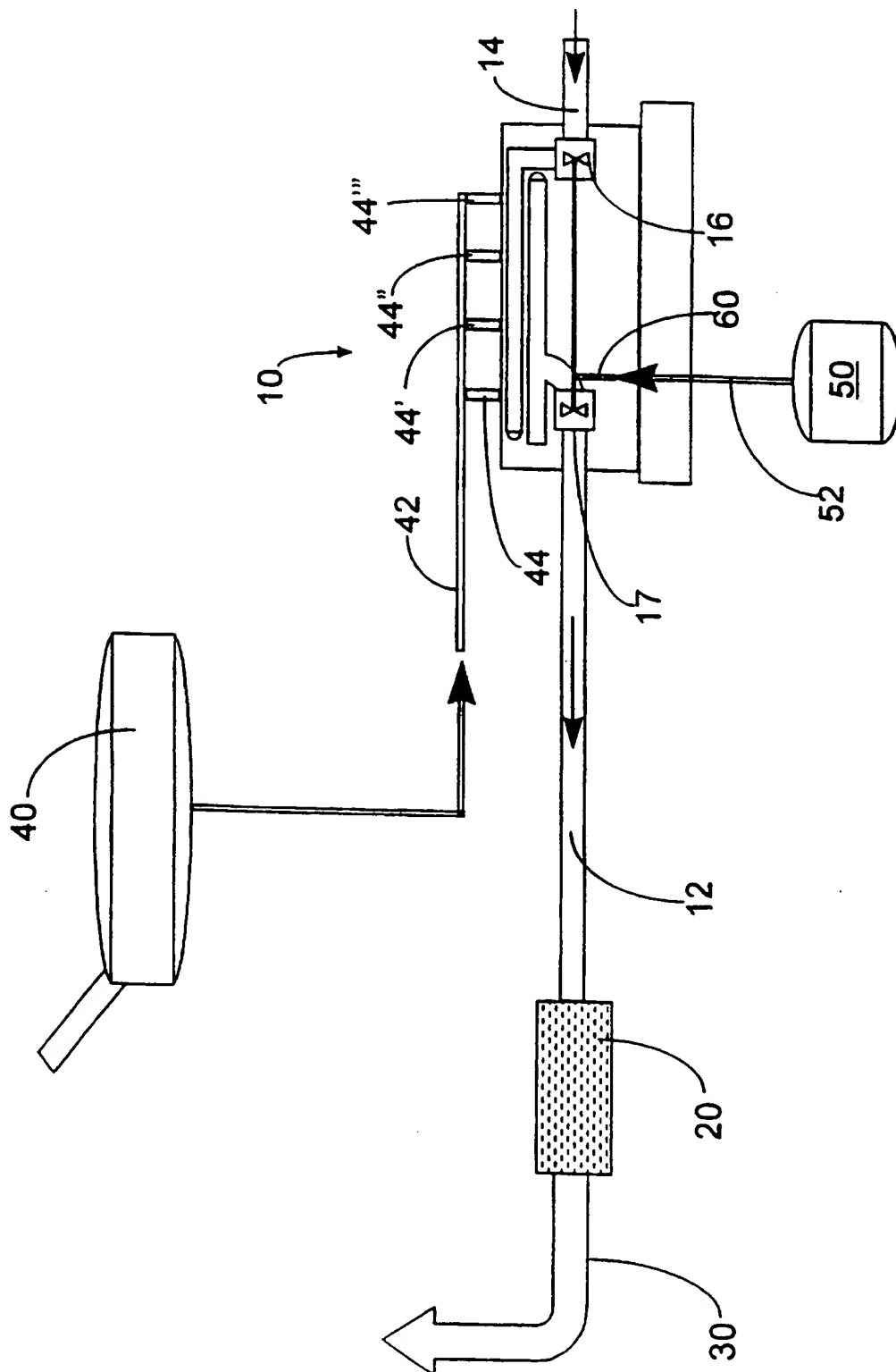


FIG. 1

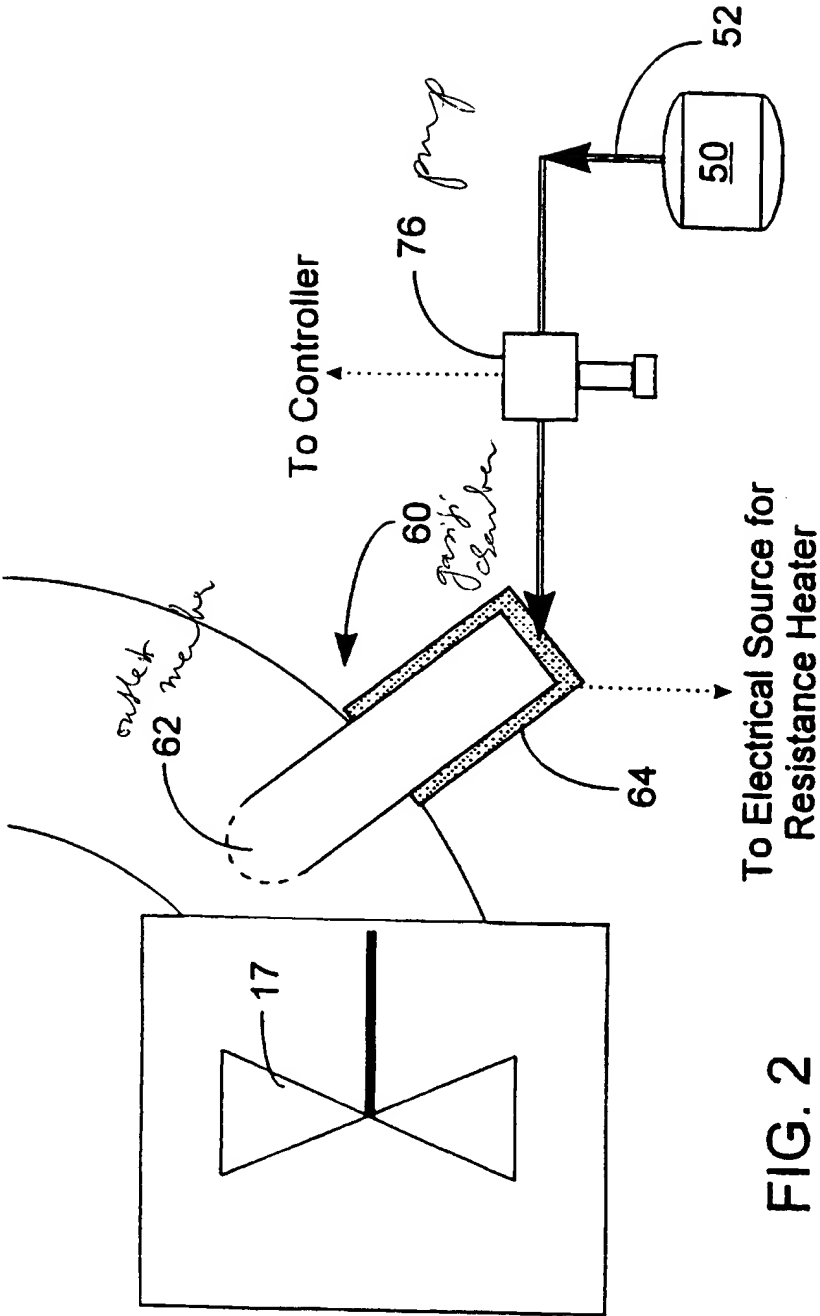


FIG. 2

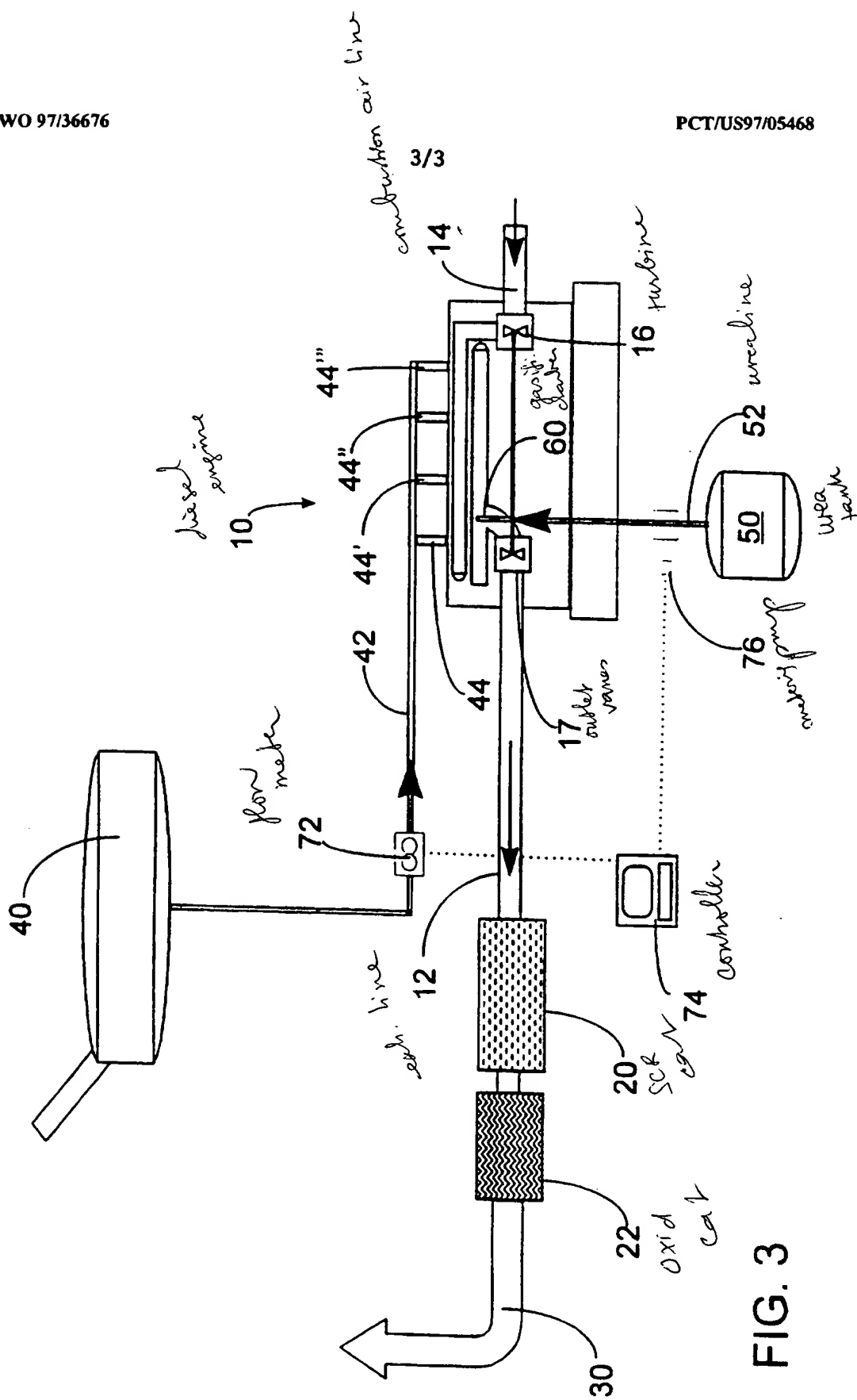
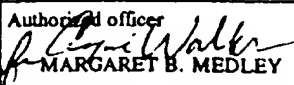


FIG. 3



## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US97/05468

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : B01J 8/00; C10B 21/00 US CL : 423/234.1, 244.09, 235 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 423/234.1, 244.09, 235; 422/169; 60/280, 301,295; 44/358,359,361,363 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,431,893 A (HUG ET AL) 11 July 1995 (11.07.95) , abstract, column 2, lines 62-end and column. 6, line 62 TO column. 7, lines 1-30.	1-20
Y	US 5,281,403 A (JONES) 25 January 1994 (25.01.94), abstract and column 4, lines 32 to column 5, lines 1-40.	1-9 and 13-14
Y	US 5,266,083 A (PETER-HOBLYN ET AL) 30 November 1993 (30.11.93), column 9, lines 43 to column 10, lines 1-39.	11-12
Y	US 4,107,272 A (MORI ET AL) 15 August 1978 (15.08.78), column 2, lines 41 to column 2, line 1-14 and claim 1.	1-7, 9 and 13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family	
Date of the actual completion of the international search 19 JUNE 1997		Date of mailing of the international search report 05 AUG 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  MARGARET B. MEDLEY Telephone No. 703-308-0661

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/05468

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,Y	US 5,601,792 A (HUG ET AL) 11 February 1997 (11.02.97) Figs, 1 and 6, column 2, lines 1-end.	1-15
E,Y	US 5,489,419 A (DIEP ET AL) 06 February 1996 (06.02.96), abstract, column 5, lines 36 to column 6, lines 1-64.	1-9 and 13
Y	US 4,138,469 A (KATO ET AL) 06 February 1979 (06.02.79), abstract, column 2, line 62 to column 3, lines 1-11 and claim 1.	1-7, 9 and 13
A	US 3,900,554 A (LYON) 19 August 1975 (19.08.75), abstract.	1-20
A	US 4,208,386 A (ARAND ET AL) 17 June 1980 (17.06.80), col. 3, lines 1-43.	1-7, 9 and 13
A	US 4,393,031 A (HENKE) 12 July 1983 (12.07.83), column 2, lines 35-end.	1-7, 9 and 13
A	US 4,997,631 A (HOFMANN ET AL) 05 March 1991 (05.03.91), column. 4, lines 29-62.	1-9 and 13
A	US 5,139,754 A (LUFTGLASS ET AL) 18 August 1992 (18.08.92), column 2, line 63 to column 4, lines 1-25.	1-9 and 13
A	US 5,057,293 A (EPPERLY ET AL) 15 October 1991 (15.10.91), column 5, lines 29-60.	1-9 and 13